THE TRANSPORT CYCLE OF ATMOSPHERIC OZONE AND ITS MEASUREMENTS FROM AIRCRAFT AND AT THE EARTH'S SURFACE

Phillip D. Falconer, Robert Pratt,
and Volker A. Mohnen
State University of New York at Albany
Albany, New York

CLASSICAL CONCEPTS OF THE TRANSPORT-DOMINATED OZONE CYCLE

The fundamental aspects of the ozone cycle, for which there appears to be solid observational documentation, may be summarized as follows:

Process 1: Photochemical production within the equatorial stratosphere

Process 2: Poleward flux of ozone through the general circulation patterns of the stratosphere

Process 3: Intrusion of ozone into the troposphere through various transport and mixing processes

Process 4: Ozone mixing within the troposphere

Process 5: Ozone destruction within the planetary boundary layer or at the Earth's surface

These mechanisms are illustrated (fig. 1) in a tentative model for large-scale ozone fluxes as suggested by Dütsch (ref. 1). It is clear that both atmospheric dynamics and photochemistry play important roles in the distribution of ozone in the atmosphere; however, this paper concentrates upon the last four phases of this cycle where recent, sometimes conflicting theories of ozone transport pathways to the troposphere have been proposed.

Process 2: Poleward Flux of Ozone in the Stratosphere

The photochemical theory of ozone predicts maximum ozone concentrations at altitudes between 20 and 30 km with the total ozone burdens in a vertical column decreasing from equator to pole and from summer to winter. However, long-term observations of total ozone indicate a distinct departure from theory with the vertical column burdens increasing toward higher latitudes and during late winter and early spring. Numerous investigators have attributed this discrepancy to atmospheric circulation patterns since the photochemical relaxation times increase rapidly downward through the stratosphere. (See fig. 2 adapted from ref. 2.) This is equivalent to saying that ozone production (and destruction) by photochemical reactions becomes so slow in the lower stratosphere that the concentration of ozone there must be largely determined by its redistribution by air currents. This also suggests that the ozone-air mixing ratio is a

quasi-conservative property of an air parcel and that ozone may therefore be used as a tracer for various scales of motion in this region. However, this general description does not indicate what types of circulations produce the ozone flux. Brewer (ref. 3) has attributed this transport exclusively to mean meridional circulations between equator and higher latitudes, but this solution is difficult to resolve with the requirement of conservation of angular momentum. Alternatively, large-scale mixing via eddy motions in the lower stratosphere would also account for the observed distribution of ozone above the tropopause, providing that poleward motion is positively correlated with sinking motion. Recent evidence from numerical simulations of ozone transport (refs. 4 and 5) shows quite clearly that the actual transport represents a strong interaction between these two modes. The task of decomposing the total (combined stratospheric and tropospheric) observed poleward ozone flux into its constitutent mean and eddy (standing and transient) components has been attempted by several investigators (refs. 6 to 11) for various seasons and across various latitude circles within the stratosphere. The reader should refer to these papers for a more complete discussion of the mathematical methodologies and data bases used. Transport within the stratosphere exclusively, however, has not been widely discussed; but, where such studies have been reported, two points may be made:

(1) The effect of mean and eddy motions exists at all latitudes. However, the net poleward ozone flux is dominated by mean meridional motions in low latitudes and by eddies in middle and high latitudes. Available evidence suggests that this lower stratospheric, transient eddy flux in middle latitudes is roughly 3 times greater during the cold season ($0.6\text{-}1.6 \times 10^7$ g-sec^{-1}) than in the warmer season ($0.2\text{-}0.6 \times 10^7$ g-sec^{-1}). (See refs. 5, 7, 8, and 12.) Mean meridional fluxes in middle latitudes are generally directed equatorward, although the magnitudes and directions have not yet been clearly established.

(2) The mid-latitude northward transport by eddies reaches a maximum in the lower stratosphere at the 10 to 14 km level. Also, observations indicate that the mean isolines of ozone mixing ratio, radioactivity, and potential vorticity have nearly the same slope in this region (refs. 13 and 7) even though each of these quantities has different source and sink regions. Because eddy motions are expected to conserve potential vorticity, they are efficient in mixing and transporting tracer materials in the stratosphere along surfaces of constant potential vorticity. The fact that these surfaces slope downward and poleward implies that ozone is carried by eddies from its equatorial source region at high altitudes to the photochemically inert lower stratosphere at high latitudes. Although the mixing ratio of ozone increases at a fixed level from equator to pole, the slope of the eddy transport pathways in the meridional direction is still consistent with the down-gradient transport of ozone (ref. 14). The details of this phenomenon are, however, still unclear. Part of the confusion lies with the interpretation of Eulerian quantities (fluxes or correlations at a fixed point or latitude); a different perspective of the transport may be gained from Lagrangian analyses from which the air motion trajectories are derived. Experiments with numerical general circulation tracer models should prove helpful in this respect (ref. 15).

Process 3: Stratospheric-Tropospheric Exchange

Although the gross aspects of this step are fairly well established, the details are relatively poorly understood, especially from a quantitative standpoint. The important property of the tropopause in the context of the ozone cycle is that it represents a nonmaterial boundary which separates well-mixed tropospheric air from the more stable air of the stratosphere. Thus, air (or ozone) which enters the troposphere is likely to experience contact with the ground within a short time. Since ozone acts as an inert tracer at tropopause levels, it is necessary to consider all processes which may result in the transfer of air from the stratosphere to the troposphere. This transfer has usually been viewed within the following categories, which generally follow those outlined by Mahlman (private communication, 1976):

(1) Intensifying upper tropospheric cyclones: Deepening upper tropospheric cyclones in the mid-latitudes are often associated with a large extrusion of stratospheric air which passes beneath the frontal jet stream and mixes with tropospheric air (refs. 16 and 17). Often the frontal zone beneath the jet stream can be considered an extension of or "fold" in the local tropopause; contained within this fold is air largely of stratospheric origin. It has been suggested that a more diffuse flow of tropospheric air into the stratosphere exists in areas adjacent to the jet stream as well.

(2) Vertical motions associated with jets and waves: Even in the absence of cyclogenetic development described in item (1), significant vertical components of motion can be associated with the upper tropospheric flow. Mahlman (ref. 18) has reviewed much of the literature on this phenomenon and has analyzed a typical case of transverse flow around a nearly straight segment of the polar front jet observed over the continental United States. Waves in the upper-level flow are also accompanied by vertical motions near the tropopause, which is a dynamically complicated region since synoptic-scale tropospheric waves are damped as they penetrate into stable stratospheric air. Such vertical motions can be important in transporting tracer substances to, if not actually through, the tropopause (ref. 19).

(3) Tropopause lifting: This process might better be described as a re-formation of the tropopause at a different level, which leads to a change in the amount of air above and below the boundary (ref. 20). Although this type of process is undoubtedly associated with seasonal variations in the radiation balance, it is difficult to include this process in a precise budget of stratospheric-tropospheric mass exchange, since the source of air which resides under the newly formed tropopause is not obvious.

(4) Mesoscale and smaller scale motions: Evidence based on radioactivity deposition indicates that severe cumulus convection can penetrate the tropopause and extract some stratospheric air (ref. 21). Gravity wave activity, either associated with this process or related to clear air turbulence situations (ref. 22), may also produce irreversible mixing across the tropopause.

(5) Mean meridional circulation: Although well-defined mathematically as the zonal mean of the meridional and vertical components of motion, the mean meridional circulation can physically represent statistical contributions from

any of the phenomena in items (1) to (4), especially in the mid-latitudes. It therefore cannot be considered as independent from the other mechanisms.

The most striking and widely accepted mechanism of ozone input to the troposphere is through cyclogenetic events (item (1)), which correlate well with the day-to-day and annual variations observed in mid-latitude surface ozone and radioactivity. However, a quantitative estimate of the annual ozone flux by this mechanism, and the others previously listed, is difficult to establish. The observational problems are the small magnitude of vertical velocities in the atmosphere, the wide range of space scales involved, and the time variability of all the mechanisms. Therefore, any estimate of the ozone flux based on meteorological data necessarily involves considerable subjectivity in order to extrapolate the annual hemispheric flux from the very limited data available.

Although estimates of ozone exchange due to large-scale eddy exchange are relatively scarce, Danielsen and Mohnen (ref. 23) and Mohnen (ref. 24) have attempted to quantify this flux by using meteorological data and representative ozone mixing ratios in the lower stratosphere. In order to establish this quantity, the authors make reference to earlier works by Danielsen[1] in which the cross-tropopause exchange of stratospheric air had been investigated. The yearly outflow rate based upon strontium-90 distributions was given as 3.6×10^{20} g(air)-yr^{-1} while, in a later study, a value of 4.3×10^{20} g(air)-yr^{-1} (e.g., 4.0×10^{17} g(air) per cyclogenetic event times a representative number of events per year) was determined. The annual ozone flux due to this process was estimated in both cases by assuming an ozone mixing ratio of 1.3×10^{-6} g-g^{-1}; this results in roughly 470×10^{12} and 560×10^{12} g-yr^{-1}, respectively (see details in ref. 23).

These various injection fluxes may be compared with estimates of the last step in the ozone cycle, destruction at the ground. The stratospheric-tropospheric exchange and destruction fluxes should agree in the classical transport cycle if the former represents the total net ozone input to the troposphere. The hemispheric ozone fluxes in the previous paragraph (multiplied by 2 for global conditions) are close to the upper limit of the latest global sink estimate in table I derived by Fabian and Pruchniewicz (ref. 25). Obviously, the meteorological estimate entails considerable subjectivity, such as the value of mean ozone mixing ratio. However, the fact remains that crude estimates based on limited meteorological data are roughly consistent with those based on the present understanding of surface destruction.

For comparison, Reiter (ref. 26) estimates the total annual mass (not specifically ozone) flux from cyclogenetic events to be only about 25 percent of Danielsen's estimate. However, the discrepancy between these authors' estimates arises from the number of cyclogenetic events per year rather than from the mass transfer per event. Reiter also estimates that the mean meridional circulation (item (5)) transfers air from stratosphere to troposphere at twice

---

[1]Although the estimates discussed in these references are based on works described in Danielsen's earlier publications, details of the estimates themselves, beyond those discussed in references 23 and 24, apparently remain unpublished.

the annual rate as cyclogenetic events (item (1)). However, his estimate of the mean circulation does not seem to account for the possibility that part of the mean flow may be contributed by cyclogenetic events in mid-latitudes, as discussed previously. Therefore, it is not at all clear that the estimates of even total mass flow by Danielsen and Reiter are in agreement.

Another type of estimate has been done by Nastrom (ref. 12) from Global Atmospheric Sampling Program data. Instead of extrapolating from case studies, he computed the average ozone concentration from a large number of aircraft measurements near the tropopause, when the large-scale flow indicated either positive or negative vertical motion. By assuming a typical large-scale vertical velocity magnitude (0.5 $cm\text{-}sec^{-1}$), he arrived at a mean ozone flux of 7.8×10^{10} $molecules\text{-}cm^{-2}\text{-}sec^{-1}$ for latitudes poleward of 30^{o} N. A reasonable conversion of this mid-latitude figure to the hemisphere yields an annual hemispheric flow a little lower than that deduced from Danielsen's detailed analysis of a single cyclogenetic event and hence well in the range of global sink estimates. Physically, Nastrom's estimate represents a very different approach in that it is based on large-scale properties rather than on the subsynoptic-scale details which are important in a folding event.

Three meteorological estimates of the cross-tropopause ozone flux have been reviewed here and all three agree roughly with surface destruction estimates. In view of the considerable simplifications necessary for these estimates and the limited understanding of the transport of air across the tropopause, it may seem fortuitous that such agreement does exist. It appears that current estimates may look right for the wrong reasons and a complete understanding of cross-tropopause transfer has yet to be achieved.

Process 4: Ozone Mixing and Transport Within the Troposphere

Ozone ingested into the troposphere from the stratosphere or any fraction which may have been produced (or destroyed) by photochemical reactions (refs. 27 and 28) is frequently assumed to be well mixed at all latitudes down to, or near the Earth's surface. The mixing efficiencies associated with the free troposphere are sufficiently large, on the average, to produce vertical ozone mixing ratio gradients perhaps an order of magnitude smaller than those found in the lower stratosphere (0 to 10 $ppbv\text{-}km^{-1}$ versus 25 to 50 $ppbv\text{-}km^{-1}$). However, on a day-to-day basis, observations show that the troposphere is not as well stirred as mean vertical ozone profiles would suggest. Ozone layers fluctuate in height or may disappear altogether on succesive days, depending upon stability and circulation patterns in the lowest 10 to 12 km of the atmosphere. Pruchniewicz (ref. 29) has illustrated these interdiurnal mixing variations in the middle troposphere (400 to 500 hPa) by using extensive ozone sounding records obtained at Boulder, Colorado (see also Dütsch et al. (ref. 30)). By comparing the ozone mixing ratios at these levels on a certain day T with the corresponding values for day T - 1 or T - 2, Pruchniewicz demonstrated the great variability of midtropospheric ozone away from the major injection and sink regions (figs. 3 and 4). The results, of course, suggest the importance of either quasi-horizontal ozone transport through the troposphere, photochemical production and destruction, or an uncertain combination of both

mechanisms. These findings therefore embody the central issues of the tropospheric ozone controversy (ref. 31).

Process 5: The Ozone Sink Near the Earth's Surface

The flux of ozone into the planetary boundary layer and to the Earth's surface is, according to classical theory, the main sink for tropospheric ozone. The rate of ozone destruction through chemical contact and reaction with various surface features, for instance, ice, water, deserts, grasslands, and forests, has been experimentally and theoretically determined (refs. 25, 32, and 33). (See table I.)

There are two points here which should be considered in connection with table I. First, the flux estimates given by various authors are generally applicable to unpolluted surface atmospheres where the effects of ozone-destructive precursors are generally eliminated. Second, according to the classical transport-dominated ozone theory, the value quoted for the mean annual ozone loss at the surface must be nearly equal to the mean annual ozone input to the troposphere. The range of estimates provided in table I is unfortunately large enough to permit a variety of interpretations on the amount of ozone exchanged across the tropopause.

AIRCRAFT OBSERVATIONS OF OZONE

Historically, aircraft measurements of atmospheric ozone may be divided into two categories: (1) those obtained from dedicated research aircraft deployed on short missions during preselected weather conditions or observing periods (refs. 23 and 34 to 37) and (2) those obtained from commercial aircraft in routine service where a variety of weather conditions along differing air routes may be encountered (refs. 38 to 40). Clearly, different analytical procedures are appropriate for each of the data sets. One common objective of aircraft ozone measurements, however, is to describe adequately the three-dimensional (latitude-longitude-height) and time variations near the injection regions and, where possible, to determine the relative importance of various ozone exchange mechanisms (cf. the section "Process 3: Stratospheric-Tropospheric Exchange").

Dedicated Research Aircraft Programs

It is safe to say that the atmospheric science community is most familiar with upper air ozone measurements obtained from dedicated aircraft missions. By and large, the information which has been recovered from these research platforms includes the details of microscale and mesoscale ozone fluctuations associated with atmospheric (e.g., temperature and wind) structure, estimates of the background tropospheric ozone content through repetitive vertical profiling, and estimates of the relative abundance of ozone-specific precursor or destruction gases (e.g., oxides of nitrogen, hydroxyl radicals) in the upper troposphere and lower stratosphere.

Perhaps one of the most interesting points of discussion in this regard involves the verification of the existence of tropopause folds beneath the jet stream core through carefully planned aircraft monitoring experiments. Although radioactive fission products were originally used as the tracers in these studies (refs. 41 and 42), ozone has proved to be an ideal species to complement these other measurements because of its quasi-conservative behavior (refs. 23, 34, and 43). From these unique sets of measurements, an important means has been isolated by which the troposphere is replenished quickly and directly with ozone from the stratosphere whenever tropopause folds develop. Danielsen and Mohnen have succinctly illustrated the structure of ozone embedded within these features (fig. 5), pointing out that the dilution of stratospheric ozone within the fold through mixing with tropospheric air is relatively slow and that ozone may occasionally reach the Earth's surface at values exceeding the current federal standards.[2]

Aircraft data have also been used to assess the average background ozone concentration between the boundary layer and the tropopause. Singh et al. (ref. 44) indicate that the average ozone mixing ratios obtained along the east coast during the summer months range between 43 and 56 ppbv (table II). Similar results have been obtained by Mohnen from measurements which he obtained aboard commercial aircraft during ascents and descents into various international airports (fig. 6). Interestingly, these records, as well as those from recent ozonesonde profiles, point to background tropospheric concentrations roughly 50 percent higher than previously reported during the 1960's by Hering and Borden (refs. 45 to 48). Clearly, a more rigorous reevaluation of the tropospheric ozone budget in light of such aircraft measurements will be increasingly called upon.

Mention should also be made of the most recent attempts in monitoring various ozone-producing or ozone-destroying trace species from aircraft platforms well above the planetary boundary layer.[3] The highly sensitive instruments required for measuring these minor constituents have been modified for flight operations in recent years, in large measure because of the cooperation of scientists around the world who participated in the federally sponsored Climatic Impact Assessment Program during the years 1972 to 1974 (ref. 49). Various spin-off monitoring programs have focused attention upon the upper troposphere as well. A brief summary of recent trace gas measurements (refs. 50 to 53) in the mid-to-upper troposphere has been compiled in table III; the reader is however encouraged to refer to the paper by Stewart, Hameed, and Pinto of this compilation for more detailed information.

---

[2]In 1970, Congress requested the U.S. Environmental Protection Agency to establish ambient air quality standards for ozone and other photochemical oxidants. The maximum ozone level, not to be exceeded for more than 1 hr, was set at 80 ppbv.

[3]Historically, most measurements of this sort have been, and continue to be, acquired from ground-based monitoring networks. This is largely due to the ultimate need within state and federal governments for establishing a sound scientific basis for oxidant control strategies.

Commercial Aircraft Measurements

Only recently has the concept of utilizing commercial aircraft in routine national or international service been tested. Depending upon the application of a particular project, experiments have been conducted either with scientific personnel on board the aircraft (refs. 23, 39, and 54) or as fully automated, unattended (refs. 55 and 56) missions. In either case, in situ measurements are, except in rare instances, a strict function of airlines' routing procedures, and therefore, many aspects of true case study research are restricted. For instance, flights into and out of the stratosphere as well as cruise altitude changes are never fully anticipated but must be accounted for in post-flight data evaluation. However, the wide and repetitive coverage offered by commercial aircraft provides a unique data base for examining ozone climate along various flight routes.

As part of an extensive ozone monitoring program supported by the Deutsche Forschungsgemeinschaft (German Science Foundation) and the Max-Planck-Institute for Chemistry, German investigators utilized numerous airliners in order to obtain upper tropospheric (10 to 12 km) ozone records (ref. 39). A flight corridor between longitudes 20° W and 35° E and extending from Norway to South Africa was established with continuous ozone registrations being acquired periodically from September 1970 through July 1973. An illustration of the tropical measurements (25° N to 25° S) has been extracted from one of their reports (figs. 7 and 8). For each season, the distribution of ozone in the tropics appears to be uniform with no systematic latitudinal variation (fig. 7). The mid-latitude data show greater variability and higher magnitudes, presumably related to the mechanisms described in the section "Process 3: Stratospheric-Tropospheric Exchange." On the other hand, there is a marked annual variation in the tropics of each hemisphere (fig. 8) with an ozone maximum in the spring months of the northern hemisphere. No detectable influence of the mean sun position upon ozone is apparent.

The Global Atmospheric Sampling Program (GASP) conceived by NASA Lewis Research Center (ref. 57) in the early 1970's is currently obtaining ozone measurements at altitudes of 6 to 13 km and latitudes 40° S to 70° N (fig. 9 taken from ref. 58). Data from these altitudes have been analyzed in a variety of fashions; the salient points of these analyses are as follows:

(1) Ozone observations obtained in the tropical upper troposphere (0° to 30° N and 50 to 100 hPa below the tropopause) are qualitatively consistent with those presented by Pruchniewicz et al. (ref. 39); that is to say that, on the average, no significant meridional gradient has been observed during the period from March 1975 to September 1976 (Falconer, unpublished data). However, an annual cycle also appears at all latitudes, which shall be discussed in the following sections. Similar conclusions may also be extracted from an analysis of the ozone distribution at 11 to 12 km by month and latitude presented by Nastrom (ref. 12). Ozone variability and its mean abundance poleward of 30° N increase sharply in the altitude range from 6 to 13 km.

(2) Zonally averaged ozone concentrations in the layer 50 to 100 hPa below the tropopause between 10° N and 60° N exhibit an annual cycle during 1975 and 1976 which shows a late fall minimum and two maxima during the spring and summer

months (ref. 38). (See fig. 10.) The cycle appears to be explained in terms of meteorological processes. The initial maximum during April begins with concommitant increases in the stratospheric ozone reservoir over mid-latitudes and in the vigor of cyclone disturbances which may transport ozone out of this reservoir. Alternatively, the prominent fall minimum arises not so much because of the weakening of cyclone exchange processes but rather because of reduced ozone content within the stratosphere. To this extent, the GASP aircraft results confirm the basic structure of the classical ozone cycle. The secondary ozone maximum during the summer probably is in part due to the rapid upward adjustment of the tropopause in late spring; ozone previously embedded within the lower stratosphere is suddenly introduced into the upper troposphere as the lifting accelerates.

(3) The space scale variability of ozone in the lower stratosphere is comparable with typical length scales for synoptic disturbances. Nastrom (ref. 12) performed lagged autocorrelation analyses upon 5-minute ozone records obtained just above the tropopause from a set of 33 carefully selected (east-west) flights. His evaluations indicated that the distance lagged correlation coefficients are crudely approximated as the product of exponential decay and a cosine variation whose half-wavelength is near 950 km. This implies a wavelength of 1900 km, typical of the east-west distance across intense ridges or troughs. He points out that the resolution of these features by ground-based or satellite measurements is unlikely.

OZONE MEASUREMENTS AT THE EARTH'S SURFACE IN REMOTE LOCATIONS

In their study of ozone variations in clean remote atmospheres, Singh et al. (ref. 44) have chosen monitoring stations which (1) were located away from urban pollution centers (at least 400 km in the case of "remote" sites) and (2) had at least a 2-year record of ozone measurements. Five stations from this work have been selected which are believed to represent ozone behavior at either mountainous or flat terrain locations.

Seasonal Variations of Surface Ozone in Rural Environments

Monthly averages of the daily ozone maxima at the Earth's surface are probably representative of the seasonal behavior of free tropospheric ozone (refs. 44, 59, and 60). These values generally occur around noon, or shortly thereafter, when vertical mixing is greatest and when the influence of the surface destruction layer is minimized. Although there appears to be a regular annual oscillation in many data records of this type, it is equally striking that many other surface ozone records in rural environments exhibit an additional, shorter term fluctuation as well. The rhythmic nature of surface ozone variations may be approximated in most instances through the application of harmonic analysis; the authors have found that the sum of the first two harmonics (e.g., annual and semiannual waves) usually accounts for at least 90 percent of the variance.

In figure 11, the annual behavior of ozone is illustrated at four remote observatories - Mauna Loa, Hawaii (19.5° N); White River, Utah (39.9° N);

Rio Blanco, Colorado (39.8° N); and Quillayute, Washington (47.9° N). All stations exhibit a rapid ozone increase (10 ppbv-month^{-1}) in spring, reaching a local maximum which ranges from March at White River to June at Rio Blanco, based on the first two harmonics. At White River and Quillayute, a second maximum occurs later in the year leading to a bimodal behavior, while Mauna Loa and Rio Blanco have more nearly a simple annual cycle.

It is instructive to examine the data in figure 11 in the context of existing models of the tropospheric ozone budget. Junge (ref. 59), Fabian (ref. 61), and Pruchniewicz (ref. 62) have developed such hemispheric or zonally averaged models based on the classical ozone cycle. The important ingredients of this type of model are stratospheric injection, surface destruction, and tropospheric ozone content, each of which is represented simply by the amplitude and phase of an annual harmonic. They also allow for a phase delay between time of maximum injection and the appearance of maximum ozone at the Earth's surface.

There is no problem with interpreting the data at Mauna Loa and Rio Blanco in terms of such a model. Each data set shows a simple annual cycle. The time of maximum ozone is different, but this could be accounted for by a latitudinal variation in the time of maximum injection and of the phase delay. Maximum injection would be expected in mid-latitudes in the late winter or spring, when the stratospheric burden of ozone is largest and cyclonic disturbances are still active. In the case of Mauna Loa, located in the subtropics, the phase delay might be considered an average time for ozone to be transported southward from the areas of strong injection in mid-latitudes.

The timing of the first ozone maximum at White River and Rio Blanco, however, is difficult to resolve in the context of a zonally averaged model. These stations are only 160 km apart. The 3-month difference in their times of maximum ozone is unlikely related to a corresponding difference in the time of maximum injection or in phase delay of the maximum, since these are intended to be large-scale properties representative of at least an entire latitude band. The bimodal nature of the White River and Quillayute records is also clearly at odds with the annual harmonic representation of simple budget models; important details of ozone variations at individual stations are unfortunately missed in these cruder mathematical approaches. Figure 12, obtained from a publication by Chatfield and Harrison (ref. 63), seems to express the inadequacies of the simple annual wave solution. The actual station records presented are, however, not necessarily inconsistent with the classical ozone transport cycle, which allows for ozone mixing and transport on various scales before it is ultimately destroyed at the Earth's surface or within the boundary layer. It is conceivable, for instance, that the secondary ozone maxima at White River and Quillayute could be attributed to late summer variations in local meteorology.

There is, however, evidence that the data presented in figures 11 and 12 could support the effects of photochemistry. Fortunately, the nitrogen oxides and hydrocarbon species records for White River and Quillayute are available for evaluating this point. At White River, where naturally occurring, nonmethane hydrocarbons are always present at concentrations of at least 100 $\mu g\text{-}m^{-3}$, nitrogen oxides concentrations rapidly increase nearly fivefold during midsummer (to approximately 50 $\mu g\text{-}m^{-3}$) and gradually decline to roughly 10 $\mu g\text{-}m^{-3}$ by the end of the year. The source for the nitrogen oxides during

the summer was not identified by Singh and his co-workers (ref. 44), but they believe that the second ozone maximum here may be indicative more of photochemical synthesis than of meteorological factors.

A similar conclusion for the secondary ozone maximum at Quillayute was not supported by the ozone precursor data records; the abundances of nitrogen oxides and hydrocarbons were found to be nonmeasurably low during this period. In the case studies of the Quillayute data, Singh et al. attribute the second warm-season maximum to long-range ozone transport from distant urban centers, such as Portland, Oregon, based upon their trajectory analyses.

Figure 13 illustrates schematically a possible explanation of how a double warm-season maximum might arise at remote mid-latitude observatories. Long-range transport of ozone from distant urban centers, or ozone synthesis in the presence of nitrogen oxides and naturally occurring, reactive hydrocarbon species, may be important (refs. 44 and 64) at stations such as White River. Dimitriades and Altshuller (ref. 65) have recently discussed the problems of quantifying the relative effects of photochemistry and transport. If the timing of the first and second peaks suggested in figure 13 is close, the resulting profile may exhibit a single delayed maximum, as does Rio Blanco (fig. 11). However, it is difficult to discriminate between photochemistry and mixing based upon the ozone records alone. If the challenge of understanding the yearly ozone cycle in clean environments is to be successfully met, a more thorough documentation of both the local meteorology and the ozone precursor behavior must be undertaken.

Diurnal Ozone Variations in Rural Environments

The daily ozone variations in clean environments depend upon the topographic setting of the monitoring station. The diurnal ozone waves which are reported at mountain locations often show small amplitude (refs. 44, 66, and 67). Also, most such records suggest that the ozone maxima are least likely to occur at noon, or shortly thereafter. On the other hand, ozone data obtained either on flat terrain or at hilltop sites generally exhibit an afternoon maximum and an early morning minimum. The diurnal ozone variations for the mountain observatories at Mauna Loa, Hawaii (19.5° N, 3400 m above mean sea level (MSL) and Whiteface Mountain, New York (44.3° N, 1510 m above MSL) will be compared with those from two nonmountain stations at Quillayute, Washington (47.9° N, 62 M above MSL) and White River, Utah (39.9° N, 1625 m above MSL).

The average daily variations at Mauna Loa and Whiteface Mountain (fig. 14) for the years indicated suggest that, in fact, the ozone maximum is almost equally probable at any time of the day, although it appears least likely in the hours surrounding noon. It is believed that these records may be interpreted in terms of the unique wind circulation characteristics of mountainous terrain (refs. 67 and 68). The limited likelihood of observing the daily ozone maximum during midday is consistent with the timing of the most vigorous upslope flow when ozone-depleted air from the rural surroundings below is brought upward along the side of the mountain. Conversely, during the evening and early morning hours when downslope flow prevails, air relatively richer in ozone is imported from above. However, a more detailed documentation of ozone in

relation to other local and larger scale wind systems in mountain areas is necessary to understand mountain data completely. There is probably considerable variation in flow characteristics among individual mountain sites.

At nonmountain stations such as Quillayute and White River (fig. 15), the daily ozone maximum generally occurs in midafternoon and the ozone minimum during the early morning hours. These characteristics agree with the well-known diurnal variation of meteorological mixing in the boundary layer. During stable conditions, vertical exchange at the top of the rural boundary layer is minimal. Ozone is isolated from its free tropospheric source aloft and is rapidly destroyed through surface contact or by chemical reactions within the shallow boundary layer. The greatest depletion of ozone appears just prior to sunrise. During the day, surface heating tends to destabilize the boundary layer, which promotes mixing of ozone from the free troposphere above down through the lower layers. This effect would, in theory, result in a midafternoon ozone maximum since the turbulent mixing would be at its peak strength at this time.

Finally, a by no means comprehensive comment is made on the prospects for interpreting ozone records obtained at clean ground-level stations and those obtained in urban-suburban locations (which have not been dealt with here). The behavior of the diurnal ozone cycle is the most likely candidate for these brief remarks since there is evidence that the afternoon ozone maximum, which may well be largely due to meteorological factors in rural settings, can also be quite plausibly related to photochemistry in urban surroundings. Conversely, boundary-layer mixing in urban environments and photochemistry (including both natural and anthropogenic precursor gases) in rural environments cannot be dismissed as important factors in the diurnal behavior at individual stations. The situation is no less complicated if the effects of ozone transport during the course of the day are considered.

The classical concept of tropospheric ozone needs no basic revision when compared with experimental findings. However, tropospheric photochemical activity involving, or producing, ozone from naturally occurring trace gases, cannot be excluded in the ozone cycle. The net destruction or production of ozone in the troposphere cannot exceed the error limits associated with the experimentally determined net flow of ozone across the tropopause and into the boundary layer. These two fluxes have been shown to be roughly comparable.

REFERENCES

1. Dütsch, H. U.: Atmospheric Ozone - A Short Review. J. Geophys. Res., vol. 75, no. 9, Mar. 20, 1970, pp. 1707-1712.

2. Grobecker, Alan J.: Progress Report on the Climatic Impact Assessment Program. Proceedings of the Third Conference on the Climatic Impact Assessment Program, Anthony J. Broderick and Thomas M. Hard, eds., DOT-TSC-OST-74-15, U.S. Dep. Transp., Nov. 1974, pp. 1-15. (Available from DDC as AD A003 846.)

3. Brewer, A. W.: The Measurement of the Vertical Distribution of Ozone and Its Meteorological Significance. Les Problèmes Météorologiques de la Stratosphère et de la Mésosphère, Presses Universitaires de France (Paris), 1966, pp. 369-382.

4. Mintz, Yale; and Schlesinger, Michael: Ozone Production and Transport With the UCLA General-Circulation Model. Proceedings of the Fourth Conference on the Climatic Impact Assessment Program, Thomas M. Hard and Anthony J. Broderick, eds., DOT-TSC-OST-75-38, U.S. Dep. Transp., Feb. 1975, pp. 201-223.

5. Cunnold, D.; Alyea, F.; Phillips, N.; and Prinn, R.: A Three-Dimensional Dynamical-Chemical Model of Atmospheric Ozone. J. Atmos. Sci., vol. 32, no. 1, Jan. 1975, pp. 170-194.

6. Newell, Reginald E.; Boer, George J.; and Dopplick, Thomas G.: Influence of the Vertical Motion Field on Ozone Concentration in the Stratosphere. Pure & Appl. Geophys., vol. 106-108, 1973, pp. 1531-1543.

7. Hering, Wayne S.: Ozone and Atmospheric Transport Processes. Tellus, vol. 18, nos. 2-3, 1966, pp. 329-336.

8. Dutsch, H. U.; and Favarger, D.: Meridional Ozone Transport by Transient Eddies Over Boulder, Colorado. Ann. Géophys., t. 25, nr. 1, 1969, pp. 219-221.

9. Hutchings, J. W.; and Farkas, Edith: The Vertical Distribution of Atmospheric Ozone Over Christchurch, New Zealand. Q. J. R. Meteorol. Soc., vol. 97, no. 412, Apr. 1971, pp. 249-254.

10. London, Julius; and Park, Jae H.: The Interaction of Ozone Photochemistry and Dynamics in the Stratosphere. A Three-Dimensional Atmospheric Model. Canadian J. Chem., vol. 52, no. 8 (pt. 2), Apr. 15, 1974, pp. 1599-1609.

11. Mahlman, J. D.: Dynamic Mechanisms Producing Large-Scale Transport of Atmospheric Trace Substances. NPS-51MZ70101A, U.S. Naval Postgraduate School, Oct. 1970. (Available from DDC as AD 719 895.)

12. Nastrom, G. D.: Vertical and Horizontal Fluxes of Ozone at the Tropopause From the First Year of GASP Data. J. Appl. Meteorol., vol. 16, no. 7, July 1977, pp. 740-744.

13. Dobson, G. M. D.: Atmospheric Ozone and the Movement of the Air in the Stratosphere. Pure & Appl. Geophys., vol. 106-108, no. 5-7, 1973, pp. 1520-1530.

14. Newell, R. E.: Transfer Through the Tropopause and Within the Stratosphere. Q. J. R. Meteorol. Soc., vol. 89, no. 380, Apr. 1963, pp. 167-204.

15. Kida, Hideji: A Numerical Investigation of the Atmospheric General Circulation and Stratospheric-Tropospheric Mass Exchange: II Lagrangian Motion of the Atmosphere. J. Meteorol. Soc. Japan, vol. 55, no. 1, Feb. 1977, pp. 71-88.

16. Danielsen, Edwin F.: Stratospheric-Tropospheric Exchange Based on Radioactivity, Ozone and Potential Vorticity. J. Atmos. Sci., vol. 25, no. 3, May 1968, pp. 502-518.

17. Reiter, Elmar R.; and Mahlman, J. D.: Heavy Radioactive Fallout Over the Southern United States, November 1962. J. Geophys. Res., vol. 70, no. 18, Sept. 15, 1965, pp. 4501-4520.

18. Mahlman, J. D.: On the Maintenance of the Polar Front Jet Stream. J. Atmos. Sci., vol. 30, no. 4, May 1973, pp. 544-557.

19. Wallace, John M.: Trajectory Slopes, Countergradient Heat Fluxes, and Mixing by Lower Stratospheric Waves. J. Atmos. Sci., vol. 35, no. 3, Mar. 1978, pp. 554-558.

20. Staley, D. O.: On the Mechanism of Mass and Radioactivity Transport From Stratosphere to Troposphere. J. Atmos. Sci., vol. 19, no. 6, Nov. 1962, pp. 450-467.

21. Reiter, E. R.; and Mahlman, J. D.: Heavy Iodine-131 Fallout Over the Midwestern United States, May 1962. Further Studies on Radioactive Fallout, Tech. Paper No. 70 (Contract AT (11-1) - 1340), Dep. Atmos. Sci., Colorado State Univ., Sept. 1965, pp. 1-53.

22. Lilly, D. K.; Waco, D. E.; and Adelfang, S. I.: Stratospheric Mixing Estimated From High-Altitude Turbulence Measurements. J. Appl. Meteorol., vol. 13, no. 4, June 1974, pp. 488-493.

23. Danielsen, Edwin F.; and Mohnen, Volker A.: Project DUSTORM Report: Ozone Measurements and Meteorological Analyses of Tropopause Folding. ASRC-SUNY-PUB-394 (Contract N00014-76-C-0283), State Univ. of New York at Albany, May 1976. (Available from DDC as AD A032 555.)

24. Mohnen, V. A.; and Reiter, E. R.: International Conference on Oxidants, 1976 - Analysis of Evidence and Viewpoints. Part III. The Issue of Stratospheric Ozone Intrusion. EPA-600/3-77-115, U.S. Environ. Prot. Agency, Dec. 1977.

25. Fabian, P.; and Pruchniewicz, P. G.: Final Report on Project "Tropospherisches Ozon." MPAE-W-100-76-21, Max-Planck-Institut Aeron., May 1976.

26. Reiter, Elmar R.: Stratospheric-Tropospheric Exchange Processes. Rev. Geophys. & Space Phys., vol. 13, no. 4, Aug. 1975, pp. 459-474.

27. Crutzen, Paul J.: Photochemical Reactions Initiated by and Influencing Ozone in Unpolluted Tropospheric Air. Tellus, vol. 26, nos. 1-2, 1974, pp. 47-57.

28. Stewart, Richard W.; Hameed, Sultan; and Pinto, Joseph P.: Photochemistry of Tropospheric Ozone. J. Geophys. Res., vol. 82, no. 21, July 20, 1977, pp. 3134-3140.

29. Pruchniewicz, Paul Gerd: Über ein Ozon-Registriergerät und Untersuchung der zeitlichen und räumlichen Variationen des Troposphärischen Ozons auf der Nordhalbkugel der Erde. Nr. 42, Max-Planck-Institut Aeron., 1970.

30. Dütsch, H. U.; Züllig, W.; and Ling, Ch.: Regular Ozone Observation at Thalwil, Switzerland and at Boulder, Colorado. LAPETH-1, Lab. Atmos. Phys., ETH, Jan. 1970.

31. Chatfield, Robert; and Harrison, Halstead: Ozone in the Remote Troposphere: Mixing Versus Photochemistry. J. Geophys. Res., vol. 81, no. 3, Jan. 20, 1976, pp. 421-423; Reply by William L. Chameides and James C. G. Walker, p. 424.

32. Aldaz, Luis: Flux Measurements of Atmospheric Ozone Over Land and Water. J. Geophys. Res., vol. 74, no. 28, Dec. 20, 1969, pp. 6943-6946.

33. Fabian, Peter; and Junge, Christian E.: Global Rate of Ozone Destruction at the Earth's Surface. Arch. Meteorol., Geophys. & Bioklimatol, Ser. A, vol. 19, no. 2, 1970, pp. 161-172.

34. Briggs, J.; and Roach, W. T.: Aircraft Observations Near Jet Streams. Q. J. R. Meteorol. Soc., vol. 89, no. 380, Apr. 1963, pp. 225-247.

35. Penn, Samuel: Temperature and Ozone Variations Near Tropopause Level Over Hurricane Isbell October 1964. J. Appl. Meteorol., vol. 5, no. 4, Aug. 1966, pp. 407-410.

36. Kuhn, Peter M.; Komhyr, Walter D.; Harris, Thomas B.; Allee, Paul A.; and Marlatt, W. E.: Observations of the Vertical Transport of Water Vapor, Ozone, and Aerosols by Thunderstorms. NOAA Tech. Rep. ERL 253-APCL 25, U.S. Dep. Commer., Feb. 1973.

37. Interhemispheric Survey of Minor Upper Atmospheric Constituents During October-November 1976. NASA TM X-73630, 1977.

38. Falconer, Phillip D.: The Global Atmospheric Sampling Program: The Prospects for Establishing a Tropospheric Ozone Budget From Commercial Aircraft Data. ASRC Publ. No. 655, State Univ. of New York at Albany, Aug. 1977.

39. Pruchniewicz, P. G.; Tiefenau, H.; Fabian, P.; Wilbrandt, P.; and Jessen, W.: The Distribution of Tropospheric Ozone From Worldwide Surface and Aircraft Observations. Proceedings of International Conference on Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations. Volume I, Int. Assoc. of Meteorol. & Atmos. Phys., 1974, pp. 439-451.

40. Osechkin, V. V.: Possibility of Investigating the Spatial Distribution of Atmospheric Ozone With the Aid of an Ozonometer Installed in the Cockpit of an Aircraft. Meteorol. & Gidrol., no. 2, Feb. 1974, pp. 103-107.

41. Danielsen, Edwin F.: Project Springfield Report. Contract DA-49-146-XZ-079, Isotopes, Inc., July 15, 1964. (Available from DDC as AD 607 980.)

42. Danielsen, E. F.; Bergman, K. H.; and Paulson, C. A.: Radioisotopes, Potential Temperature and Potential Vorticity - A Study of Stratospheric-Tropospheric Exchange Processes. Dep. Meteorol. & Climatol., Univ. of Washington, 1962.

43. Danielsen, E.; Bleck, R.; Shedlovsky, J.; Wartburg, A.; Haagenson, P.; and Pollock, W.: Observed Distribution of Radioactivity, Ozone, and Potential Vorticity Associated With Tropopause Folding. J. Geophys. Res., vol. 75, no. 12, Apr. 20, 1970, pp. 2353-2361.

44. Singh, Hanwant B.; Ludwig, Francis L.; and Johnson, Warren B.: Ozone in Clean Remote Atmospheres: Concentrations and Variabilities. CRC-APRAC CAPA-15-76, Coord. Res. Counc., Inc., June 1977. (Available from NTIS as PB 272 290.)

45. Hering, Wayne S., ed.: Ozonesonde Observations Over North America. Vol. I. AFCRL-64-30(1), U.S. Air Force, Jan. 1964. (Available from DDC as AD 435 873.)

46. Hering, Wayne S.; and Borden, Thomas R., Jr., eds.: Ozonesonde Observations Over North America. Vol. 2. AFCRL-64-30(II), U.S. Air Force, July 1964. (Available from DDC as AD 604 880.)

47. Hering, Wayne S.; and Borden, Thomas R., Jr.: Ozonesonde Observations Over North America. Vol. 3. AFCRL-64-30(III), U.S. Air Force, Aug. 1965. (Available from DDC as AD 623 018.)

48. Hering, Wayne S.; and Borden, Thomas R., Jr.: Ozonesonde Observations Over North America. Vol. 4. AFCRL-64-30(IV), U.S. Air Force, Dec. 1967. (Available from DDC as AD 666 436.)

49. The Natural Stratosphere of 1974. CIAP Monograph 1. DOT-TST-75-51, U.S. Dep. Transp., Sept. 1975. (Available from NTIS as PB 246 318.)

50. Goldan, P. D.; Bush, Y. A.; Fehsenfeld, F. C.; Albritton, D. L.; Crutzen, P. J.; Schmeltekopf, A. L.; and Ferguson, E. E.: Tropospheric N_2O Mixing Ratio Measurements. J. Geophys. Res., vol. 83, no. C2, Feb. 20, 1978, pp. 935-939.

51. Inn, Edward C. Y.; Tyson, Bennett J.; and Arvesen, John C.: Atmospheric Halocarbon Experiment. Interhemispheric Survey of Minor Upper Atmospheric Constituents During October-November 1976. NASA TM X-73630, 1977, pp. 79-93.

52. Davis, D. D.; Heaps, W.; and McGee, T.: Direct Measurements of Natural Tropospheric Levels of OH Via an Aircraft Borne Tunable Dye Laser. Geophys. Res. Lett., vol. 3, no. 6, June 1976, pp. 331-333.

53. Stedman, D. H.; Ritter, J.; and Kelly, T.: Measurements of Background Levels of Tropospheric NO_x. Univ. of Michigan paper presented before the Division of Environmental Chemistry, American Chemical Society (Anaheim, California), Mar. 1978.

54. Bischof, Walter: Ozone Measurements in Jet Airliner Cabin Air. Water, Air, & Soil Pollut., vol. 2, no. 1, Mar. 1973, pp. 3-14.

55. Perkins, Porter J.: Global Measurements of Gaseous and Aerosol Trace Species in the Upper Troposphere and Lower Stratosphere From Daily Flights of 747 Airliners. NASA TM X-73544, 1976.

56. Holdeman, James D.; and Falconer, Phillip D.: Analysis of Atmospheric Ozone Measurements Made From a B-747 Airliner During March 1975. NASA TN D-8311, 1976.

57. Steinberg, Robert: Role of Commercial Aircraft in Global Monitoring Systems. Science, vol. 180, no. 4084, Apr. 27, 1973, pp. 375-380.

58. Holdeman, J. D.; Nastrom, G. D.; and Falconer, P. D.: An Analysis of the First Two Years of GASP Data. NASA TM-73817, 1977.

59. Junge, Christian E.: Global Ozone Budget and Exchange Between Stratosphere and Troposphere. Tellus, vol. 14, no. 4, Nov. 1962, pp. 363-377.

60. Fabian, P.; and Pruchniewicz, P. G.: Meridional Distribution of Ozone in the Troposphere and Its Seasonal Variations. J. Geophys. Res., vol. 82, no. 15, May 20, 1977, pp. 2063-2073.

61. Fabian, P.: A Theoretical Investigation of Tropospheric Ozone and Stratospheric-Tropospheric Exchange Processes. Pure & Appl. Geophys., vol. 106-108, no. 5-7, 1973, pp. 1044-1057.

62. Pruchniewicz, P. G.: The Average Tropospheric Ozone Content and Its Variation With Season and Latitude as a Result of the Global Ozone Circulation. Pure & Appl. Geophys., vol. 106-108, no. 5-7, 1973, pp. 1058-1073.

63. Chatfield, Robert; and Harrison, Halstead: Tropospheric Ozone. 2. Variations Along a Meridional Band. J. Geophys. Res., vol. 82, no. 37, Dec. 20, 1977, pp. 5969-5976.

64. Chatfield, R.; and Rasmussen, R. A.: An Assessment of the Continental Lower Tropospheric Ozone Budget. International Conference on Photochemical Oxidant Pollution and Its Control. Proceedings: Volume I, Basil Dimitriades, ed., EPA-600/3-77-001a, U.S. Environ. Prot. Agency, Jan. 1977, pp. 121-136. (Available from NTIS as PB-264 232.)

65. Dimitriades, Basil; and Altshuller, A. Paul: International Conference on Oxidant Problems: Analysis of the Evidence/Viewpoints Presented. Part I. Definition of Key Issues. J. Air Pollut. Control Assoc., vol. 27, no. 4, Apr. 1977, pp. 299-307.

66. Lovill, James E.: Note on the Variability of Ozone at a High Mountain Location. Arch. Meteorol., Geophys. & Bioklimatol, Ser. A, vol. 19, no. 4, 1970, pp. 439-442.

67. Mohnen, V. A.; Hogan, A.; Whitby, R.; and Coffey, P.: Ozone Measurements in Rural Areas. State Univ. of New York at Albany paper presented at Symposium on the Non-Urban Tropospheric Composition (Hollywood, Florida), Nov. 1976. (Available from DDC as AD A037 360.)

68. Mendonca, Bernard G.: Local Wind Circulation on the Slopes of Mauna Loa. J. Appl. Meteorol., vol. 8, no. 4, Aug. 1969, pp. 533-541.

TABLE I.- ESTIMATES OF THE GLOBAL SINK FOR ATMOSPHERIC OZONE

BY VARIOUS AUTHORS

Author	Data base	Global sink estimate, 10^{12} g-yr^{-1}
Lettau (1951)[a]	Not specified	51
Paetzold (1955)[a]	Not specified	320 to 640
Kroening & Ney (1962)[a]	Vertical profiles near the Earth's surface	770
Junge (1962)[a]	From theoretical model prediction	470
Brewer & Wilson (1968)[a]	Photochemical calculations	750
Aldaz (1969)[a]	Experimental	1300 to 2100
Fabian & Junge (1970) (ref. 33)	From theoretical model prediction	400 to 710
Fabian & Pruchniewicz (1976) (ref. 25)	From theoretical model prediction	479 to 931

[a]Destruction flux rates quoted have been adapted from data compilation by Fabian and Junge (ref. 33).

TABLE II.- AIRCRAFT MEASUREMENTS OF OZONE IN THE FREE TROPOSPHERE (ABOVE THE PLANETARY BOUNDARY LAYER)

[From Singh et al. (ref. 44)]

Locations	Dates	Sources	Average O_3 concentrations (free troposphere), ppbv	Number of flights considered
Canton, Ohio	July 2-22, 1976	Washington State University at Pullman	51 ± 13	10
Groton, Conn.	July 15-30, 1975	Washington State University at Pullman	43 ± 10	21
	August 6-19, 1975	Washington State University at Pullman	51 ± 14	16
Boston, Mass.	August 12-27, 1975	U.S. Environmental Protection Agency	56 ± 8	30
New Brunswick, N.J. (and vicinity)	August 10-20, 1975	Interstate Sanitation Commission of New York	53 ± 14	62
Bridgford, Conn. (and vicinity)	July 20-27, 1975	Battelle Columbus Lab.	56 ± 8	5
	August 5-20, 1975	Battelle Columbus Lab.	56 ± 9	5

TABLE III.- RECENT TROPOSPHERIC MEASUREMENTS OF OZONE-REACTIVE SPECIES FROM DEDICATED RESEARCH PLATFORMS

Compound	Reaction chain	Data base	Abundance in free troposphere, ppbv	Reference
N_2O	$N_2O + O(^1D) \rightarrow 2NO$ $NO + O_3 \rightarrow NO_2 + O_2$	Interhemispheric survey at 7 to 17 km; six parachute descent profiles	318 ± 2 (Approximate)	50
			306 ± 21 (Northern Hemisphere)	51
			314 ± 39 (Southern Hemisphere)	51
OH	$OH + O_3 \rightarrow O_2 + HO_2$	Several aircraft flights during October 1975 at 21° N and 32° N	0.28 to 0.70 (Approximate)	52
NO	$NO + O_3 \rightarrow NO_2 + O_2$ $NO + \dot{R}O_2 \rightarrow NO_2 + \dot{R}O$	Measurements obtained at Fritz Peak, Colo.	0.1 to 0.3	53

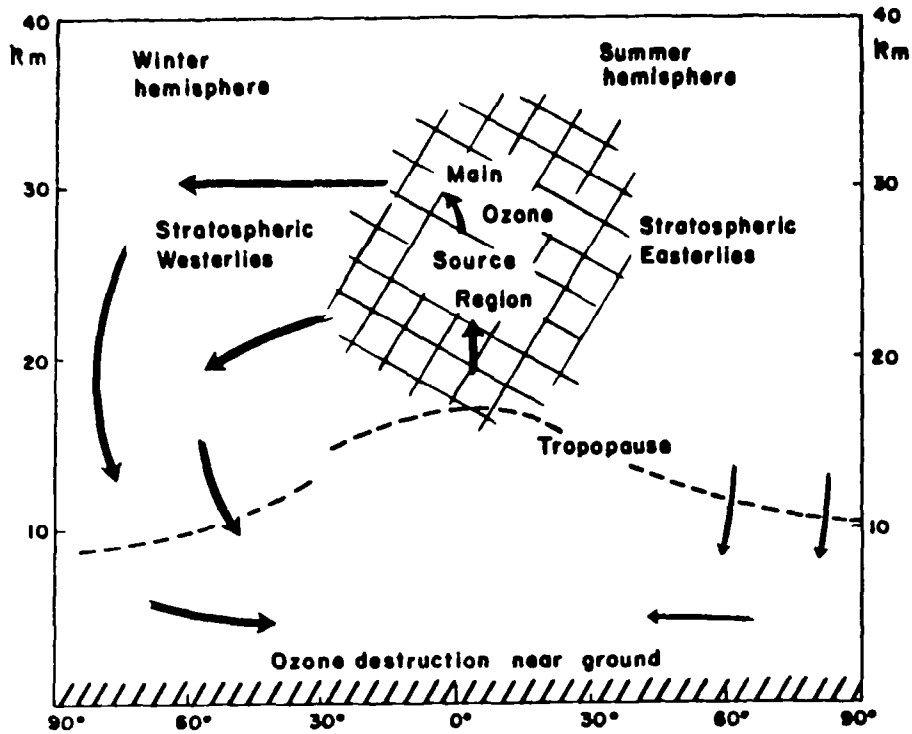


Figure 1.- Tentative model of large-scale ozone fluxes and of seasonal ozone cycle. (From Dütsch (ref. 1), copyrighted by American Geophysical Union; reproduced with permission.)

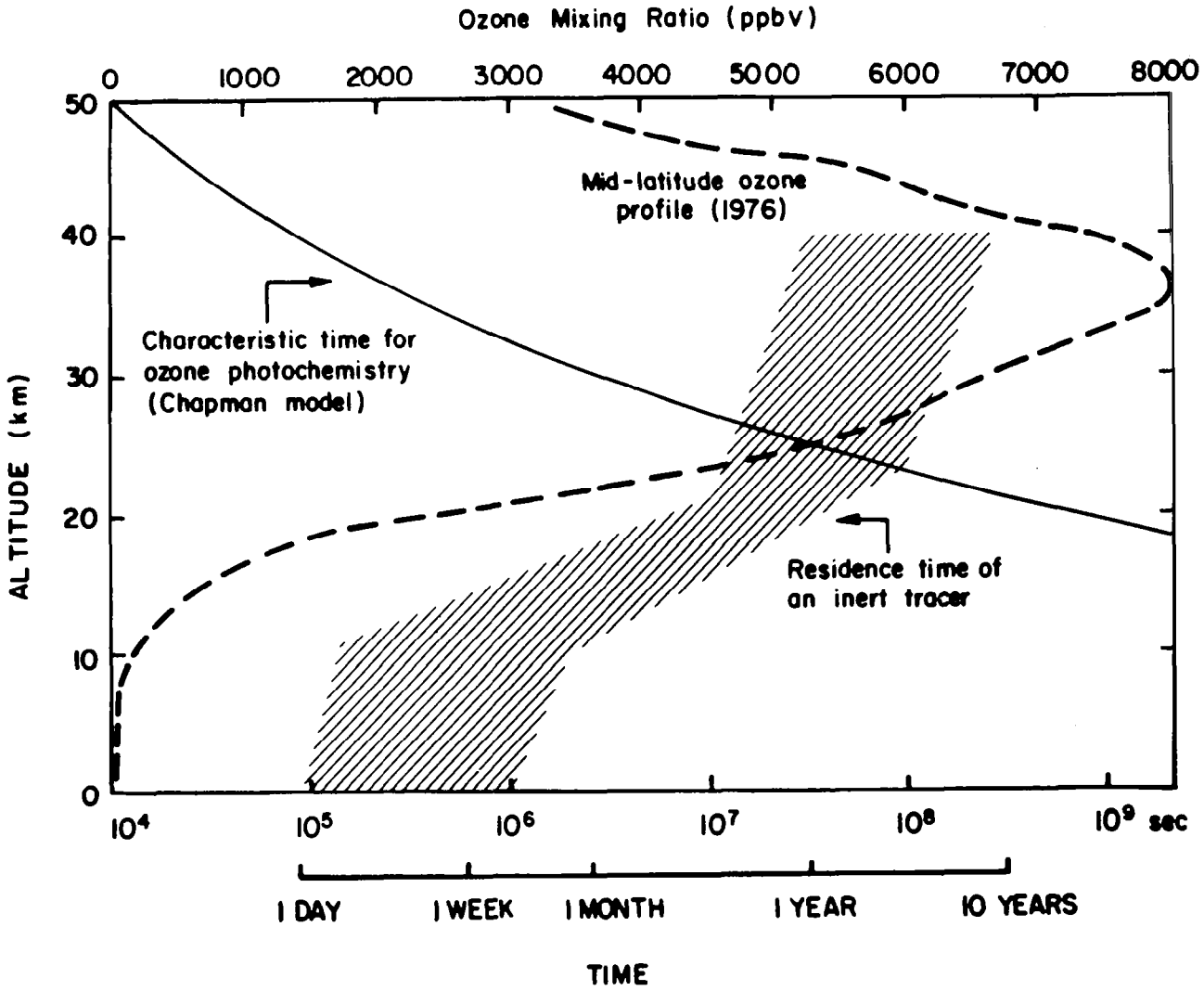


Figure 2.- Characteristic time scales for chemistry and motions in the atmosphere. (Adapted from ref. 2.)

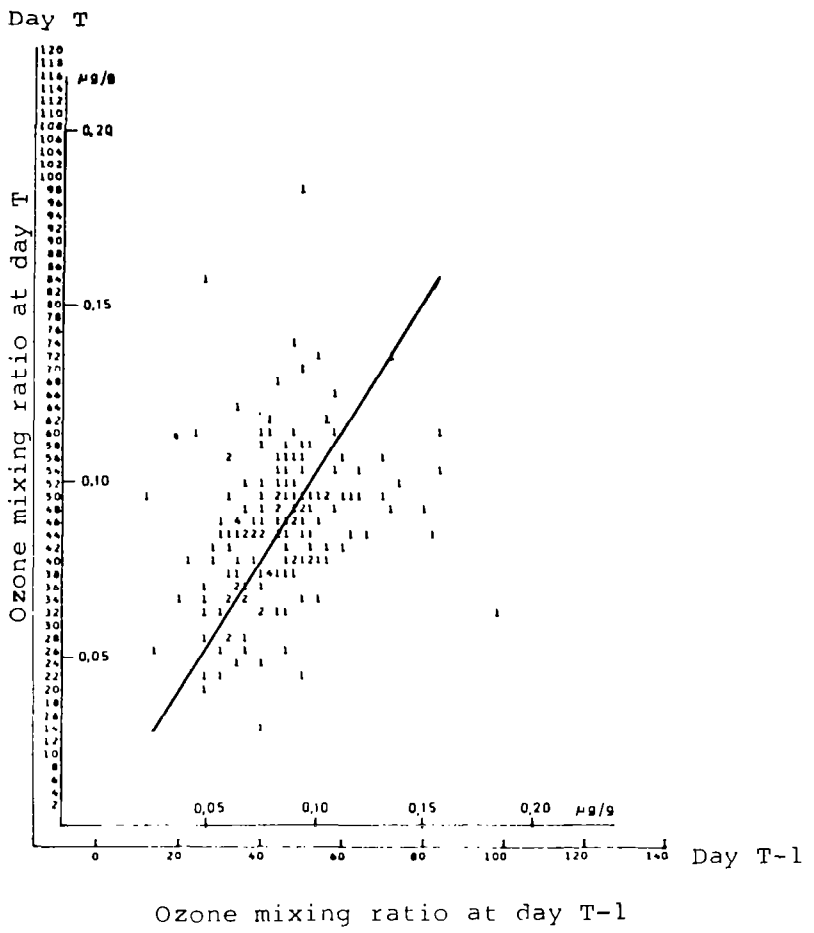


Figure 3.- Correlation between ozone mixing ratio on day T with that on day T - 1 at 400 hPa and 500 hPa levels over Boulder, Colorado. Each of 161 data points consists of a pair of values for days T and T - 1. (From Pruchniewicz (ref. 29) with permission of publisher.)

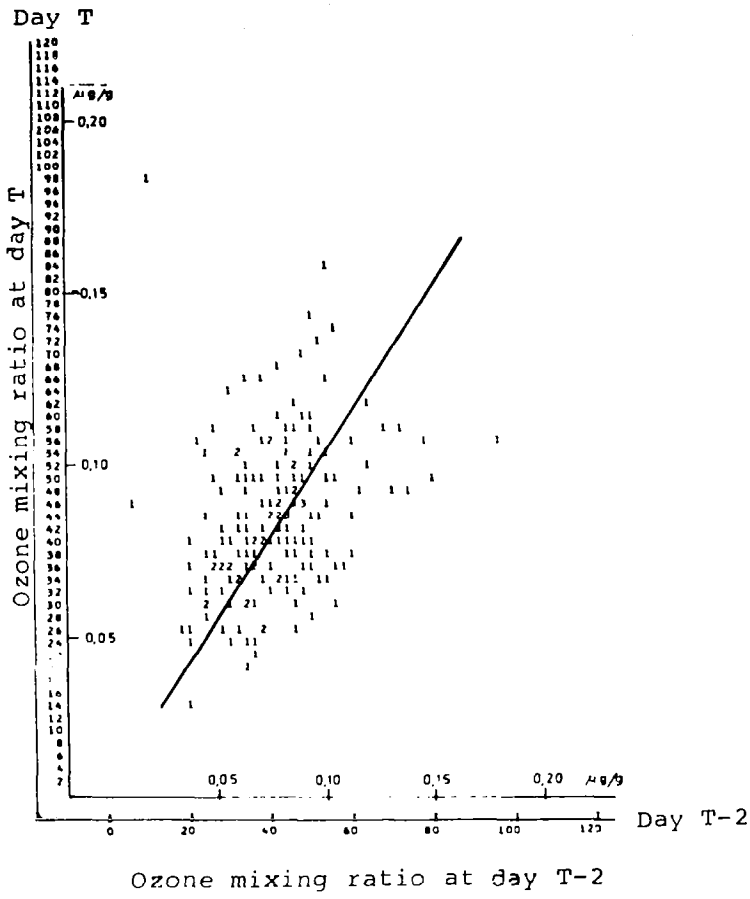
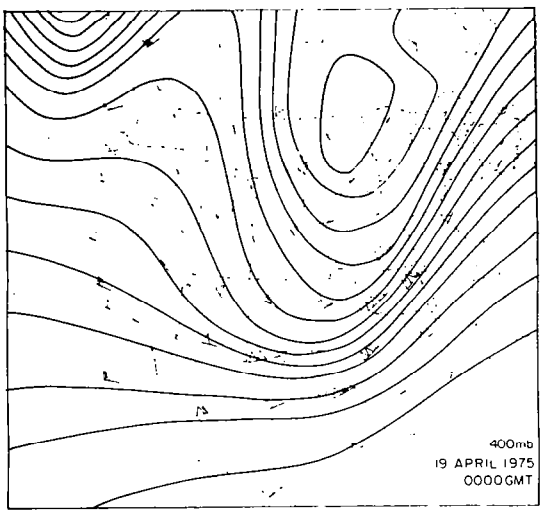
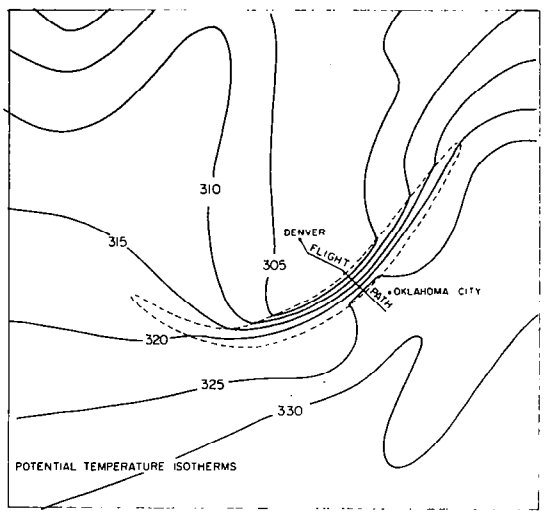


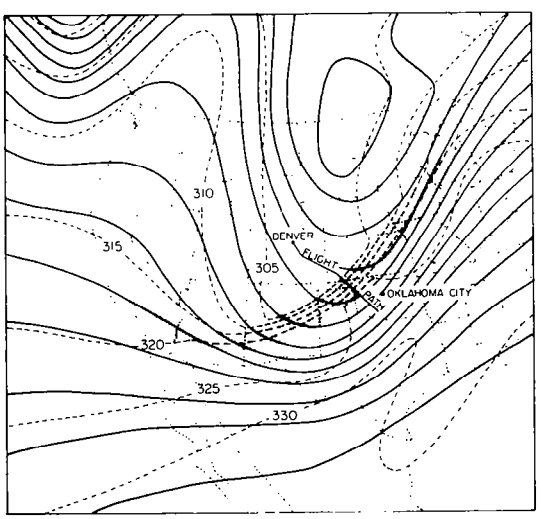
Figure 4.- Correlation between ozone mixing ratio on day T with that on day T - 2 at 400 hPa and 500 hPa levels over Boulder, Colorado. Each of 174 data points consists of a pair of values for days T and T - 2. (From Pruchniewicz (ref. 29) with permission of publisher.)



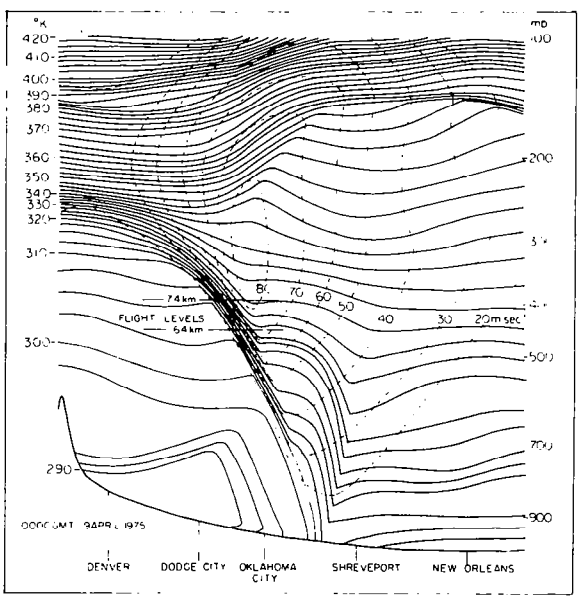
(a) 400 hPa (mb) height field.



(b) Potential temperature isotherms in K at 400 hPa.

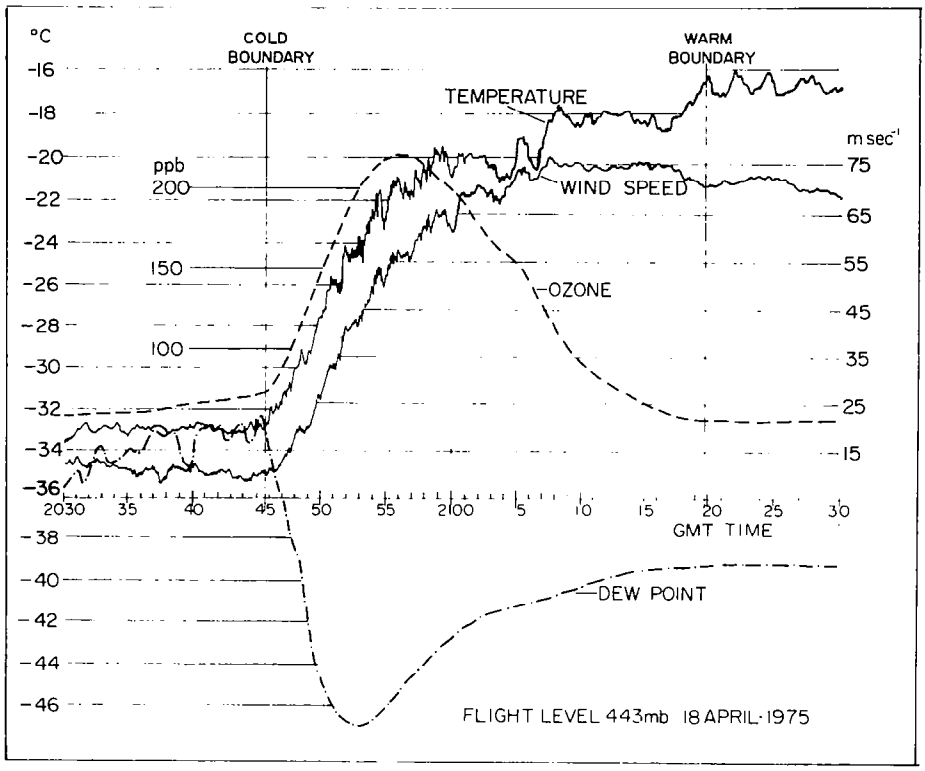


(c) Intersection of folded tropopause with 400 hPa surface.



(d) Vertical cross section of potential temperature (solid lines) and wind speed (dotted lines).

Figure 5.- Meteorological conditions at 00:00 GMT, April 19, 1975, in the upper troposphere associated with tropopause foldings. (From Danielsen and Mohnen (ref. 23).)



(e) Measurements of ozone and other meteorological variables across folded tropopause at flight level of 443 hPa from the National Center for Atmospheric Research Electra aircraft.

Figure 5.- Concluded.

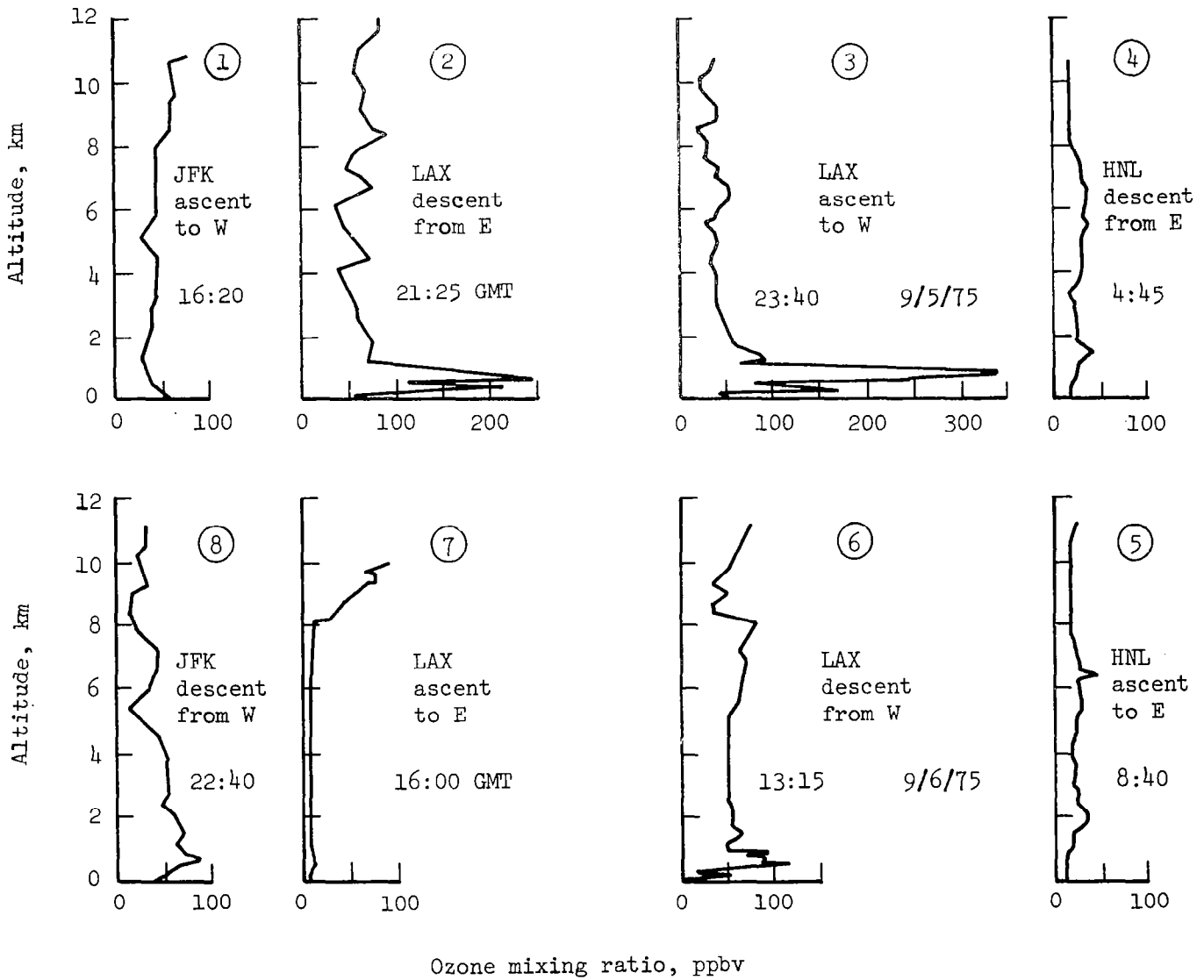


Figure 6.- Vertical ozone mixing ratio profiles obtained on September 5 and 6, 1975, aboard commercial aircraft during ascent from or descent into New York City (JFK), Los Angeles (LAX), and Honolulu (HNL). (From V. Mohnen, unpublished data.)

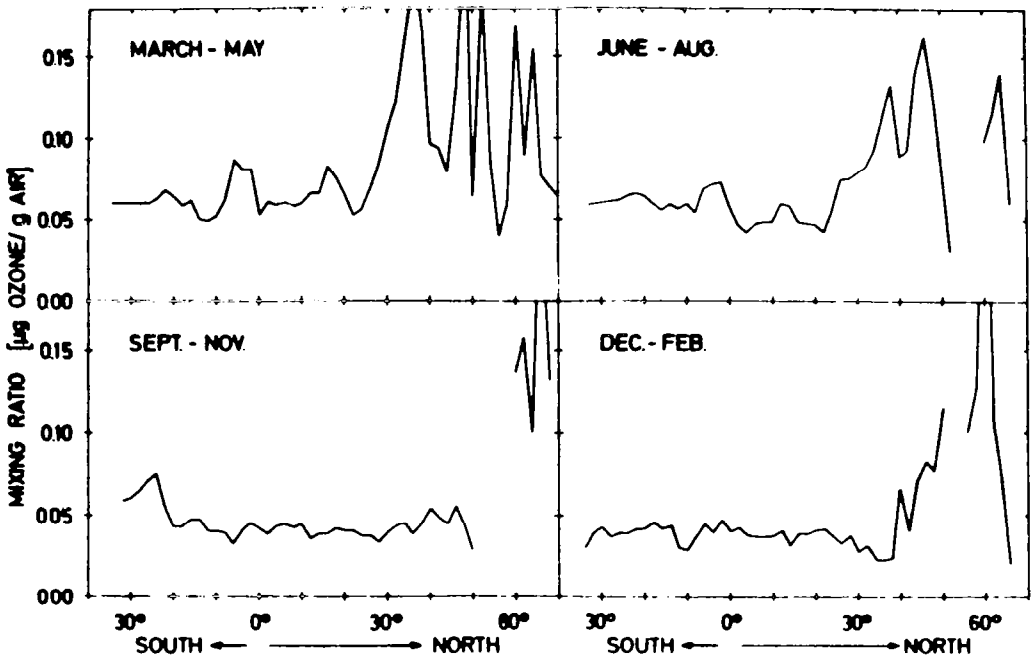


Figure 7.- Latitudinal profiles of mean ozone mixing ratio in four 3-month intervals from aircraft measurements over Europe and Africa. (From Pruchniewicz et al. (ref. 39).)

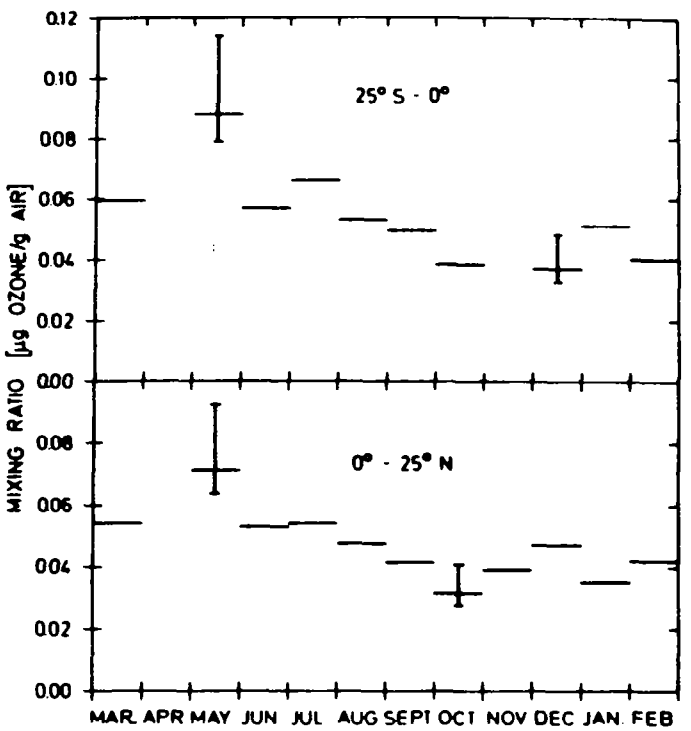


Figure 8.- Seasonal variation of monthly mean tropospheric ozone from aircraft measurements between 25° N and 25° S. (From Pruchniewicz et al. (ref. 39).)

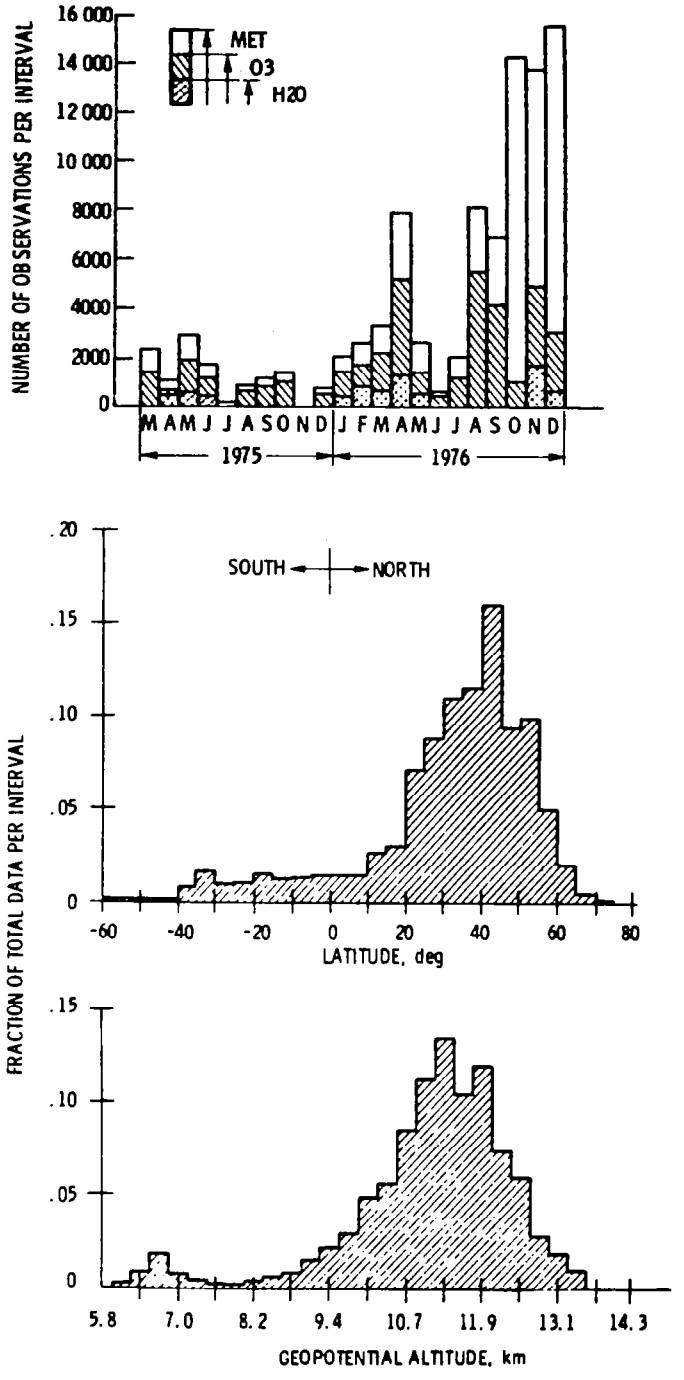
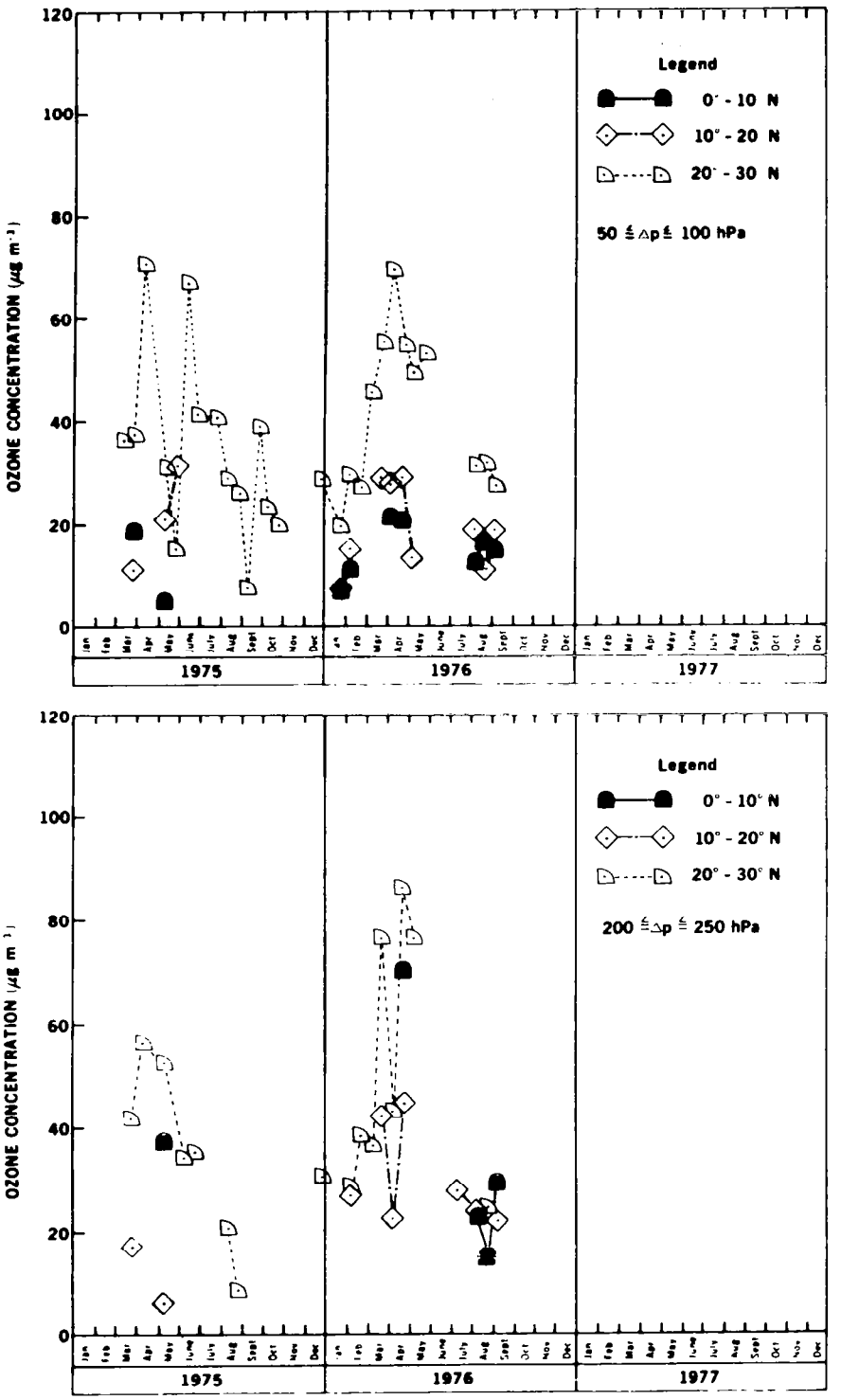
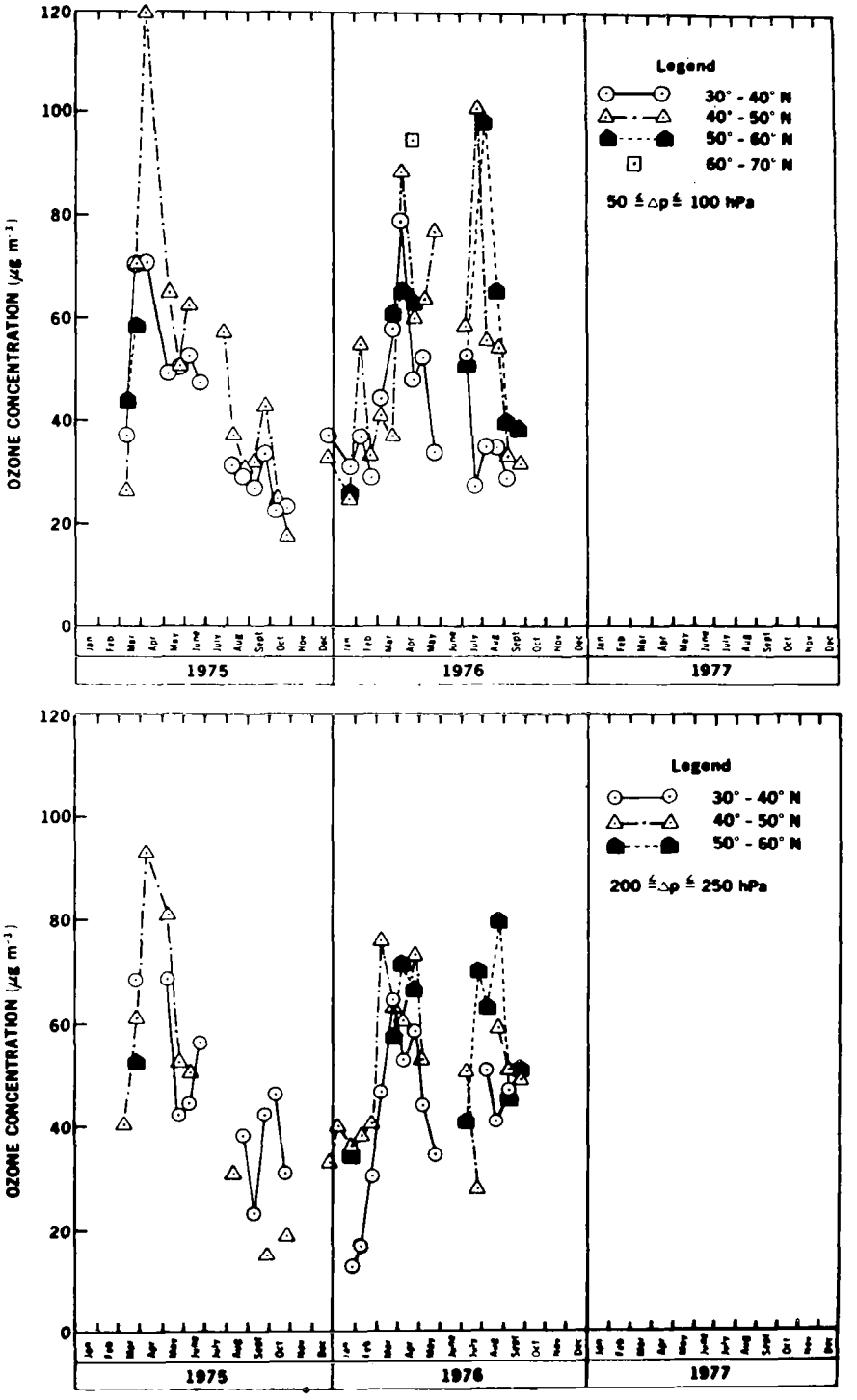


Figure 9.- Distribution of flight and meteorological (MET), ozone (O3), and water vapor (H2O) data by month, latitude, and altitude from commercial B-747 airliners participating in the Global Atmospheric Sampling Program. (From ref. 58.)



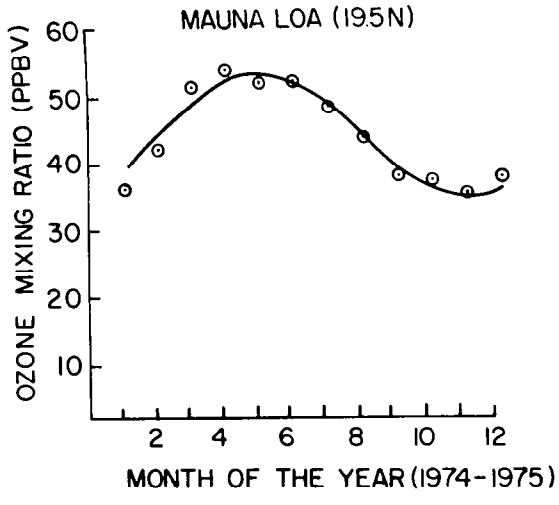
(a) Between 0° N and 30° N.

Figure 10.- Biweekly ozone concentrations ($\mu g\text{-}m^{-3}$) obtained aboard participating GASP airliners for two pressure intervals, 50 to 100 hPa below tropopause and 200 to 250 hPa below tropopause.

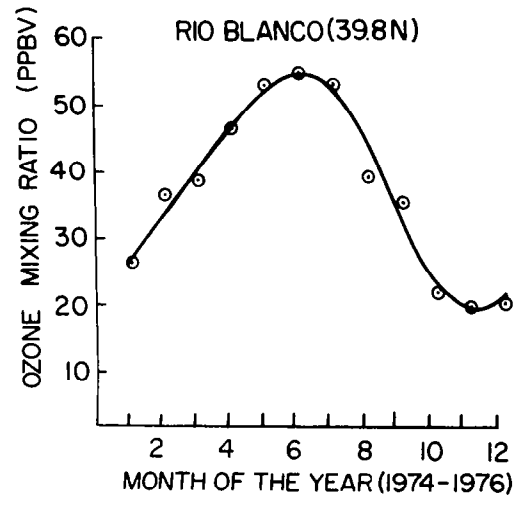


(b) Between 30° N and 70° N.

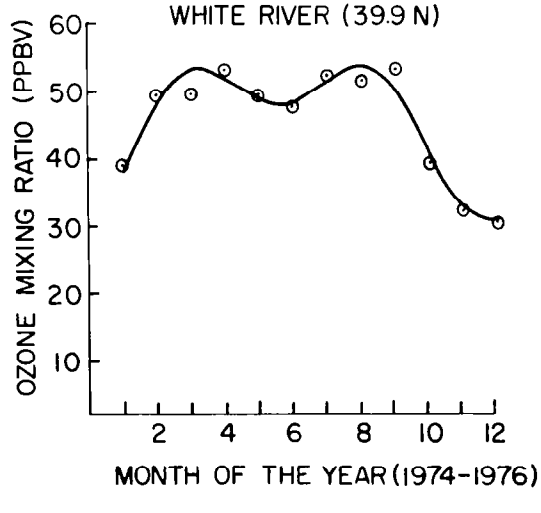
Figure 10.- Concluded.



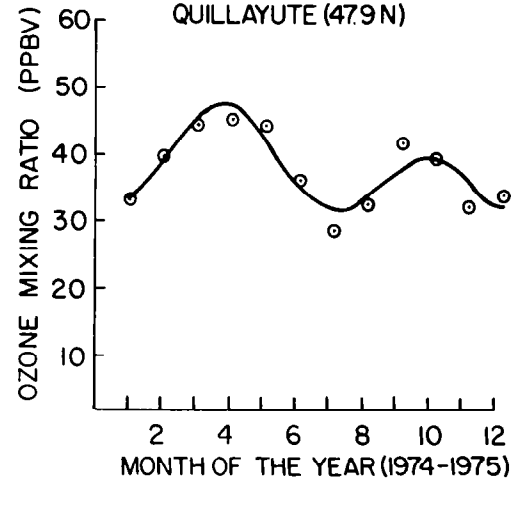
(a) At Mauna Loa, Hawaii.



(b) At Rio Blanco, Colorado.



(c) At White River, Utah.



(d) At Quillayute, Washington.

Figure 11.- Variations of monthly averages of daily 1-hour ozone maxima for the years 1974 and 1976. Individual data points have been interpolated from Singh et al. (ref. 44) and fitted by a smoothed harmonic function representing sum of annual and semiannual waves.

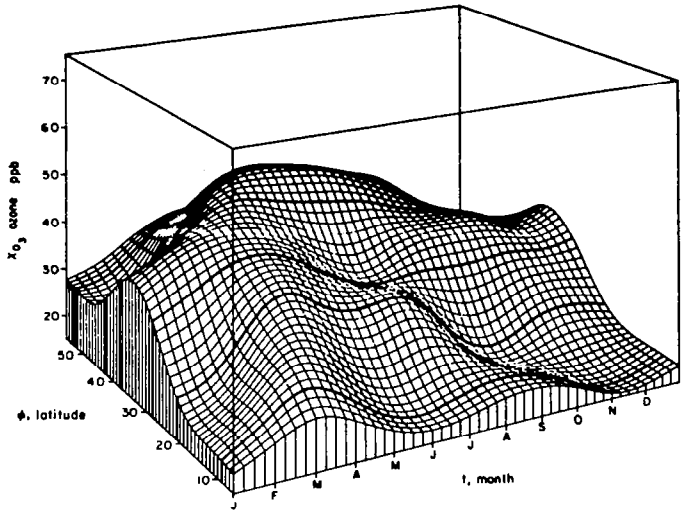


Figure 12.- Latitude-season perspective of ozone mixing ratios at 2 to 3 km above six stations near 75° W longitude. (From Chatfield and Harrison (ref. 63), copyrighted by American Geophysical Union; reproduced with permission.)

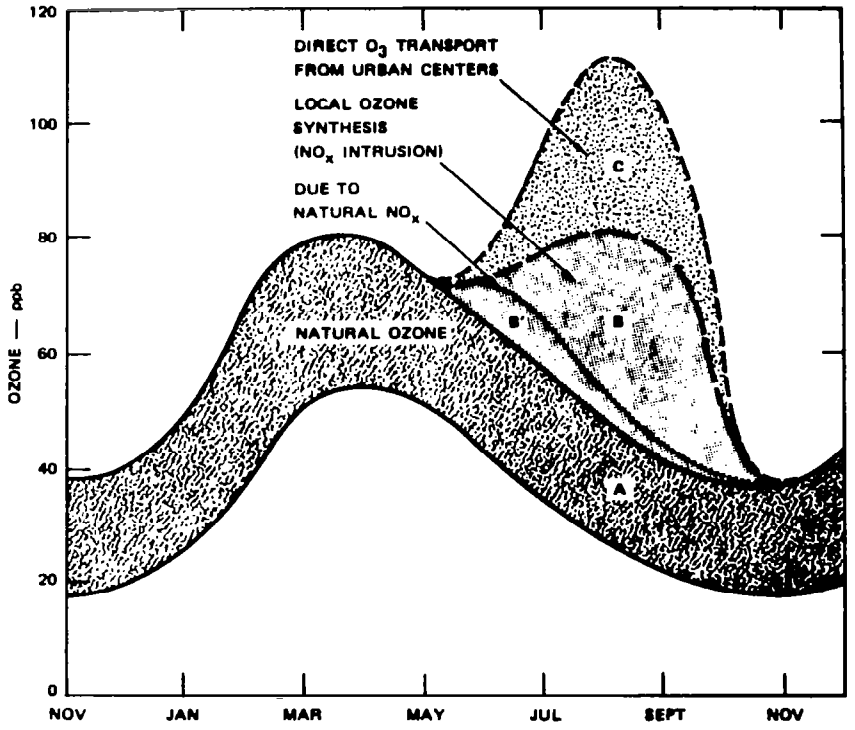


Figure 13.- Idealized sketch of ozone variations at remote observatories. (From Singh et al. (ref. 44).)

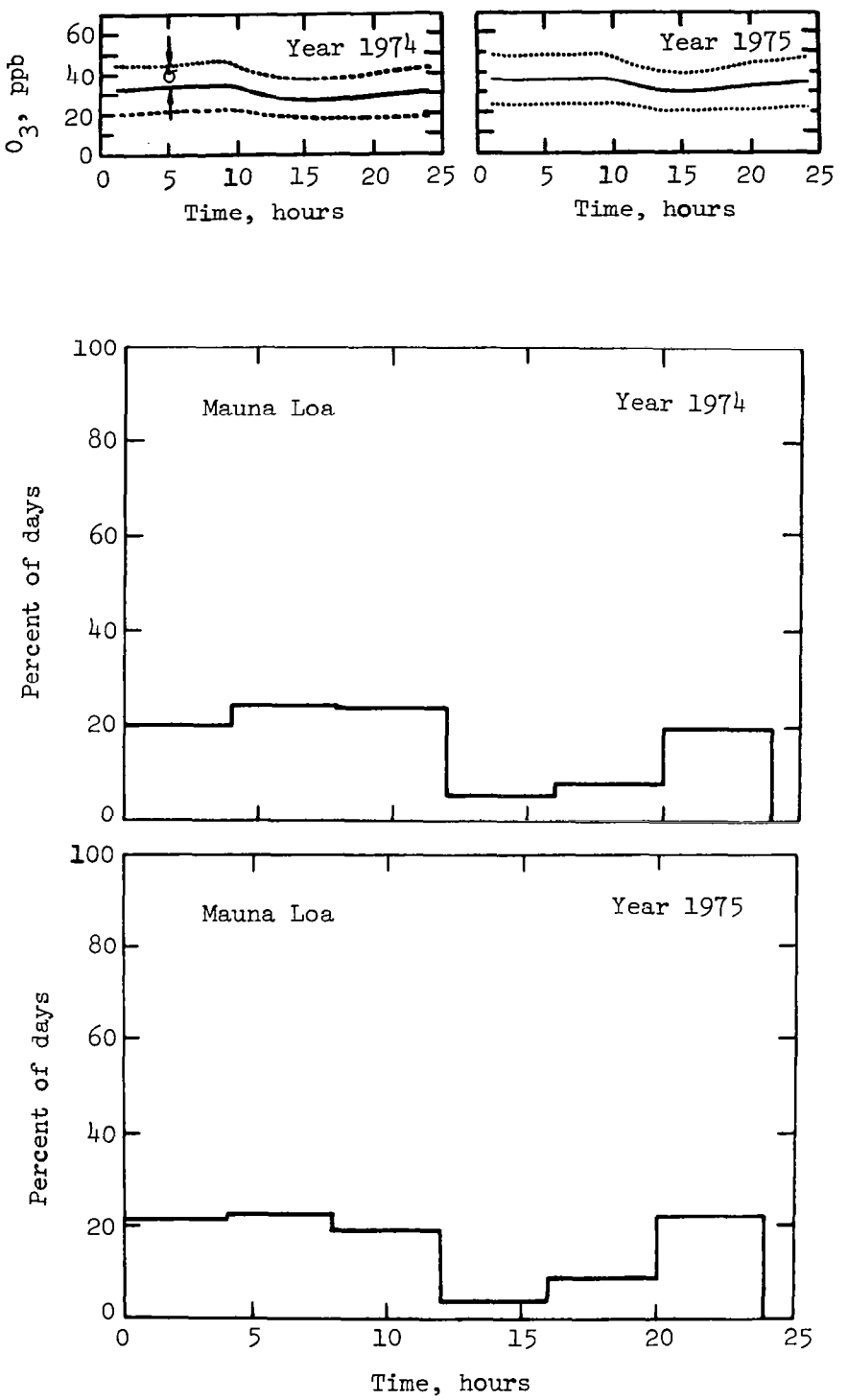
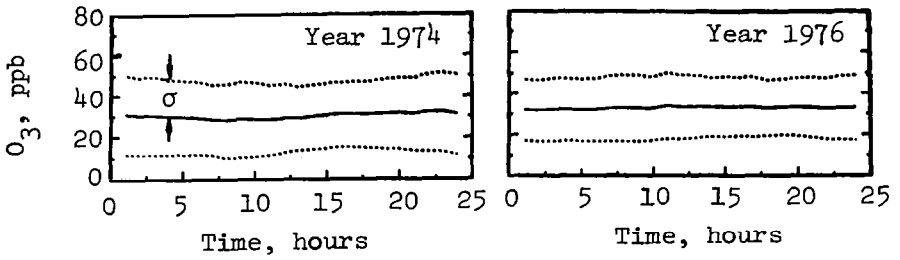
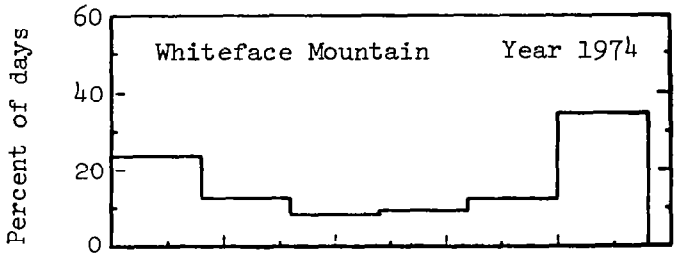


Figure 14.- Yearly average diurnal ozone variations and frequency distributions of daily 1-hour ozone maxima at Mauna Loa, Hawaii, and Whiteface Mountain, New York. Both stations are representative of mountain ozone behavior in rural environments. (From Singh et al. (ref. 44).)





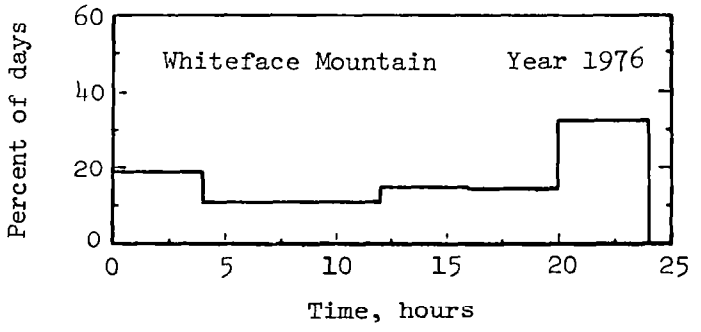


Figure 14.- Concluded.

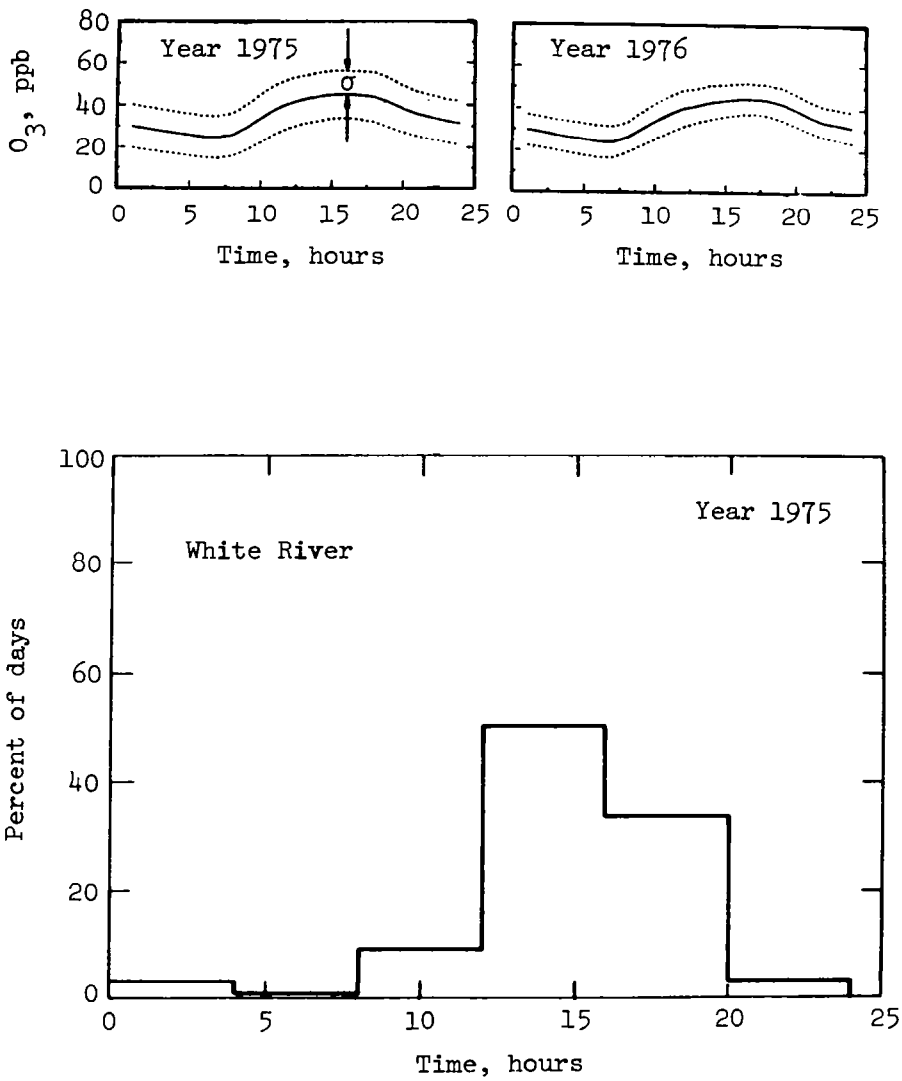
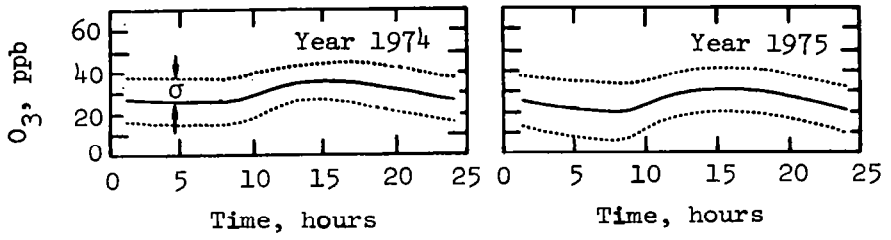


Figure 15.- Yearly average diurnal ozone variations and frequency distributions of daily 1-hour ozone maxima at Quillayute, Washington, and White River, Utah. Both stations are representative of ground-level ozone behavior in rural environments. (From Singh et al. (ref. 44).)



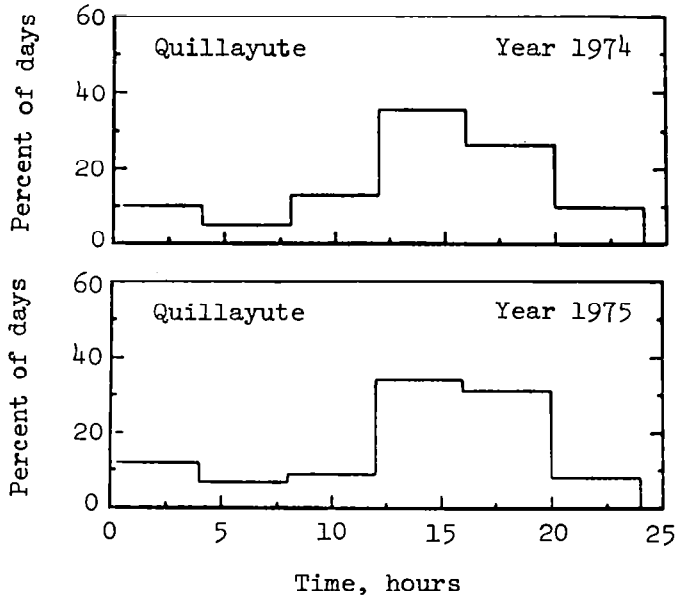


Figure 15.- Concluded.